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INSTITUTE OF ENERGY CONVERSION

UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

February 20, 2008

Bolko von Roedern
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12
D.5.24

Dear Bolko,

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of October 1, 2007 to October 31, 2007, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS-based solar cells).

Task 2 – CIS-based Solar Cells

Roll-to-Roll Deposition of $Cu(InGa)Se_2$ at Different Web Speeds

During this period the effort proceeded in two directions. In the first case a substrate carrier was installed in the roll-to-roll system. The purpose of the carrier was to allow in-line deposition on both glass (rigid) and polyimide (flexible) substrates. Furthermore, using 4" to 6" of polyimide coupon per run is more cost effective than using 5' to 6' of material in each experiment. The carrier was tested with soda lime (SL) glass substrate at a temperature of 550°C and with polyimide substrate at a temperature of 450°C. All other parameters were kept constant. Table I, below, gives the device efficiencies and the deposition parameters for the two substrates. On SL glass substrate Cu/(Ga+In) and Ga/(Ga+In) were measured to be 0.9 and 0.3 respectively.

Table I. Deposition parameters and device performance of $Cu(InGa)Se_2$ deposited on SL glass and polyimide substrate using the substrate carrier.

Run Number	Substr. Material	Speed (in./min.)	CIGS Thick. (μm)	Eff %	Subs. T (°C)	Cu T (°C)	Ga T (°C)	In T (°C)	Se T (°C)
70455.1	SL glass	1.0	2.06	15.8	550	1364	1133	1053	350
70471.2	Upilex	1.0	1.54	9.1	450	1374	1133	1033	350

These ratios on the polyimide substrate were found to be 0.95 and 0.35 respectively. V_{OC}, J_{SC}, and FF of the devices were 0.619V, 34.5 mA/cm^2, and 74.1% on SL glass while they were 0.575V, 28.4 mA/cm^2, and 55.8% on polyimide. Surface structure of the Cu(InGa)Se_2 films are shown in Figure 1.

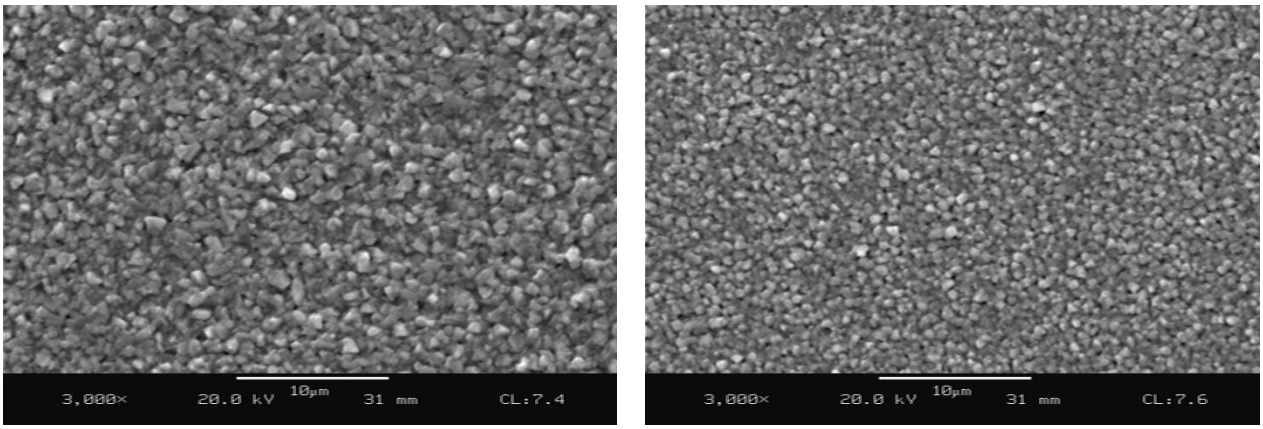


Figure 1. Surface structure of the Cu(InGa)Se_2 films deposited on SL glass at 550°C (left) and on Upilex at 450°C (right). Note the better developed grain structure at high temperature on SL glass.

The other direction the effort was pursued was in the development of a Na source for incorporation into the in-line system. To that effect, an evaporation source identical to those used in the in-line system was installed in bell-jar type vacuum system. The evaporative characteristics of NaF from the source is presently being evaluated. When the quantitative picture is developed the information will be transferred to the NaF source that is being installed into the in-line system.

Improved Performance with Absorber Thickness < 1 µm

The overall objective of this task is to develop methods to increase J_{SC} in devices using absorber layers with thickness d ≤ 1.0 µm. Cu(InGa)Se_2 cells have been demonstrated with no significant loss in V_{OC} and FF using absorber layers ≤ 0.7 µm and low J_{SC} has been identified as the primary loss factor.[1,2] In this report, we present results of our implementation of light scattering in Cu(InGa)Se_2 devices and evaluate its potential for increasing J_{SC}.

Our approach for light scattering is to texture the TCO layer using a post-deposition etch of sputtered ZnO films as has been implemented for a-Si devices.[3] For Cu(InGa)Se_2 solar cells, TCO deposition or post-deposition treatment should be performed at temperatures no higher than 200°C to maintain the integrity of the underlying junction. In this report we show that ITO films can be textured using an HCl etch and we report efforts to implement this into the processing of Cu(InGa)Se_2 cells.

ITO films were deposited on glass substrates using rf sputtering with thickness ~ 500 nm and sheet resistance 10 - 12 Ω/sq. This is triple the thickness used for baseline device processing at IEC. Films were etched in dilute HCl at different conditions: concentrations from 5 – 50%,

temperatures from 25 – 60°C, and times up to 120 s. Films were characterized by sheet resistance (R_{sh}), optical transmittance (T), and AFM to determine surface morphology. Optical scattering is determined by the haze factor defined by $T_{diffuse} / T_{total}$ which were measured using an integrating sphere attachment on the optical spectrophotometer and averaged over the wavelength range $600 \leq \lambda \leq 1000$ nm. AFM images are shown in Figure 2 for the as-deposited ITO and after etching in 10% HCl for 10 s at ~25°C. This etched film had R_{sh} =19 Ω/sq and haze = 9.7% compared to haze = 2.3 % in the as-deposited film. Similar values of R_{sh} and haze could be obtained with different concentrations and temperatures.

Preliminary tests were performed to determine if the etching could be successfully done on devices. For this purpose the baseline glass / Mo / Cu(InGa)Se_2 / CdS / ZnO / ITO / grid device structure was used with the as-deposited ITO thickness increased to 500 nm. After ITO deposition, the edges of the sample were masked using nail polish and then the samples were etched under different conditions. The nail polish was removed and grids were deposited. All devices were either shorted or had very low current as shown, for example, for the 6 devices on one sample in Figure 3. The cause of the low current has not yet been determined.

Experiments were also done with etching ZnO films. However, these were less successful than ITO in producing a significant increase in haze. The films used were deposited at room temperature and had poor crystallinity, unlike the films deposited in ref. 2 which were deposited at temperatures up to 300°C.

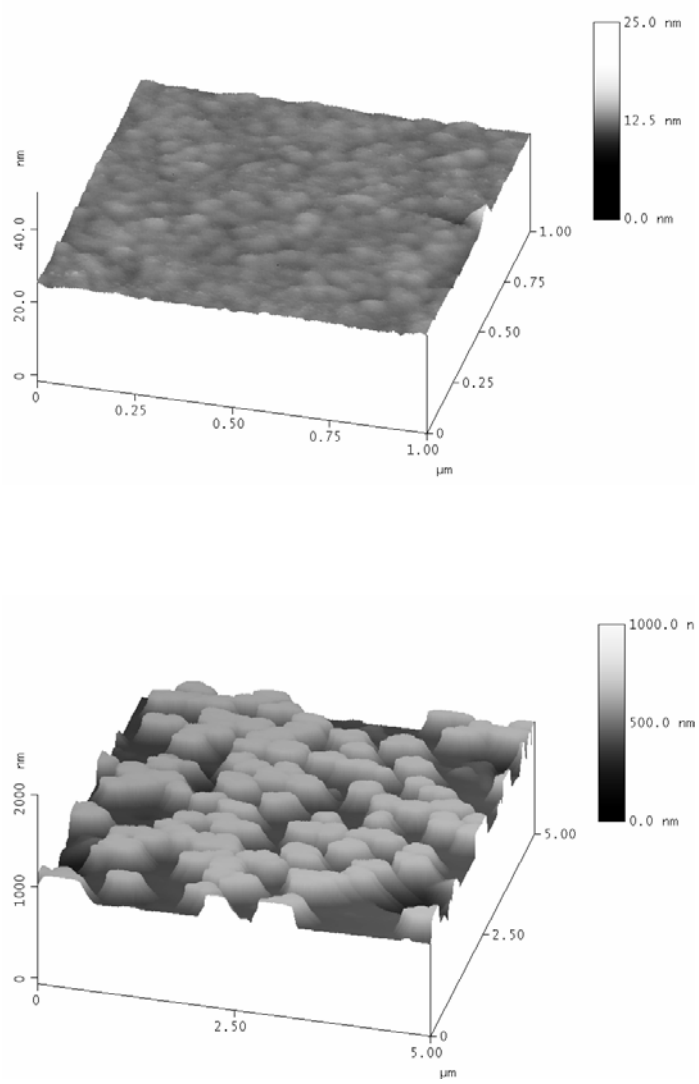


Figure 2. AFM images of (top) an as-deposited ITO film and (bottom) after etching in 10% HCl for 10 s at ~25°C.

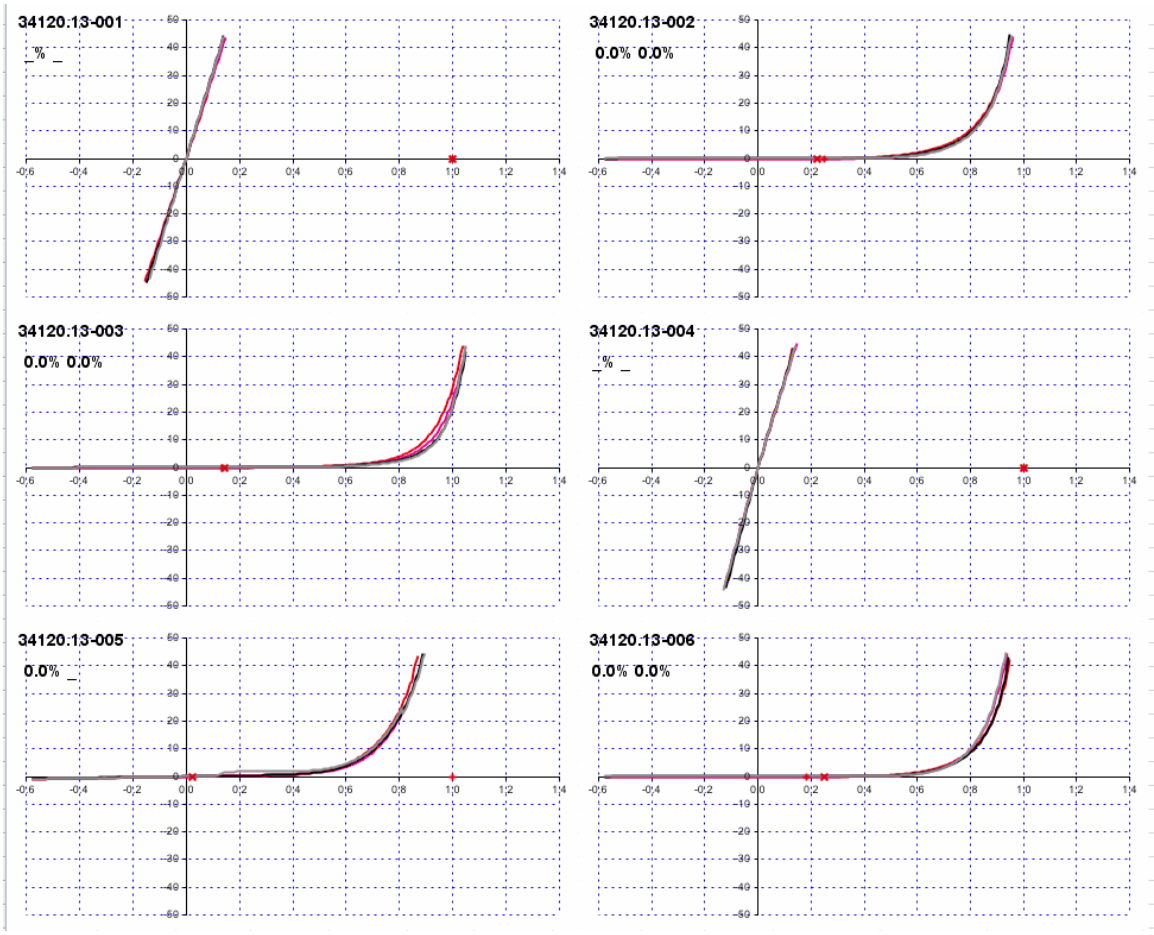


Figure 3. J-V curves for 6 Cu(InGa)Se_2 cells on a sample with etch-textured ITO.

Composition Control for Increased V_{OC}

In this task we are investigating the processes to increase V_{OC} in Cu(InGa)$(SeS)_2$ solar cells by controlling film growth and composition. Specifically, methods are being developed to control the relative through-film Ga composition in the formation of Cu(InGa)$(SeS)_2$ films from the reaction of metal precursors by circumventing the formation of Cu-Ga-In intermetallic phases using mixed metal/metal-selenide precursors.

In the present, precursors containing copper selenide were prepared. Films with the CuSe phase were formed by electrochemical deposition onto Mo-coated soda-lime glass substrates. To obtain the $Cu_{2-x}Se$ phase, a 60 minute anneal at 300ºC under vacuum was performed. Ga and In were e-beam evaporated onto the copper selenide films to yield Cu/(In+Ga) = 0.9 and Ga/(In+Ga) = 0.3 in the precursors. As a control, $Cu_{0.8}Ga_{0.2}$/In precursors with a composition of Cu/(In+Ga) = 0.9 and Ga/(In+Ga) = 0.2 were prepared by sequential sputtering. In all films, thicknesses were chosen to give a final 2 µm thick Cu(InGa)Se_2 film. The precursors were selenized for 5, 15 or 90 min at 450ºC at atmospheric pressure in a quartz tube reactor using a 0.35at% H_2Se/0.0035at% O_2/Ar gas mixture.

The selenized films were characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS) and x-ray diffraction (XRD) using CuKα1 incident radiation from the top surface of the films. The backside of the films and Mo surface were analyzed after peeling the films at the interface between Cu(InGa)Se_2 and Mo. Solar cells with a device structure of glass/Mo/Cu(InGa)Se_2/CdS/ZnO:ITO/Ni:Al grid were fabricated. Current-voltage (J-V) characteristics and external quantum efficiency (EQE) curves of the solar cells were measured.

XRD measurements indicate that the selenization reaction rates for the two copper selenide precursors are faster than for the $Cu_{0.8}Ga_{0.2}$/In precursor. After 5 min selenization, intermetallic Cu_3Ga and $Cu_9(GaIn)_4$, as well as InSe and Cu(InGa)Se_2 phases were identified by XRD for the films made from $Cu_{0.8}Ga_{0.2}$/In precursors. In contrast, only the InSe phase was identified along with Cu(InGa)Se_2 for the films made from CuSe/Ga/In and $Cu_{2-x}Se$/Ga/In precursors. After 15 min selenization, only Cu(InGa)Se_2 was seen in the XRD plots for the two copper selenide precursors, but Cu_9Ga_4 was still present for the $Cu_{0.8}Ga_{0.2}$/In precursor. After 90 min selenization, a $MoSe_2$ phase was observed for the CuSe/Ga/In precursor in addition to Cu(InGa)Se_2.

Cu(InGa)Se_2 (112) peaks from XRD plots of films after 90 min selenization are shown in Figure 4. Broader peaks indicate a broader Ga distribution in the Cu(InGa)Se_2 chalcopyrite structure for the films made from CuSe/Ga/In and $Cu_{2-x}Se$/Ga/In precursors compared to the control with $Cu_{0.8}Ga_{0.2}$/In precursors.

Ga/(In+Ga) ratios measured by EDS from the top and backside of the films after 5, 15, and 90 min selenizations are shown in Figure 5. The films made from $Cu_{2-x}Se$/Ga/In precursors show a more homogeneous Ga distribution than the control. In contrast, the films made from CuSe/Ga/In precursors show a higher Ga concentration in the front half of the film than in the back. While the high Ga concentration at the back for metallic precursors can be explained by the reaction preference of Se with the Cu-In intermetallic over that of Cu-Ga, the higher Ga at the front for CuSe/Ga/In precursors is not understood.

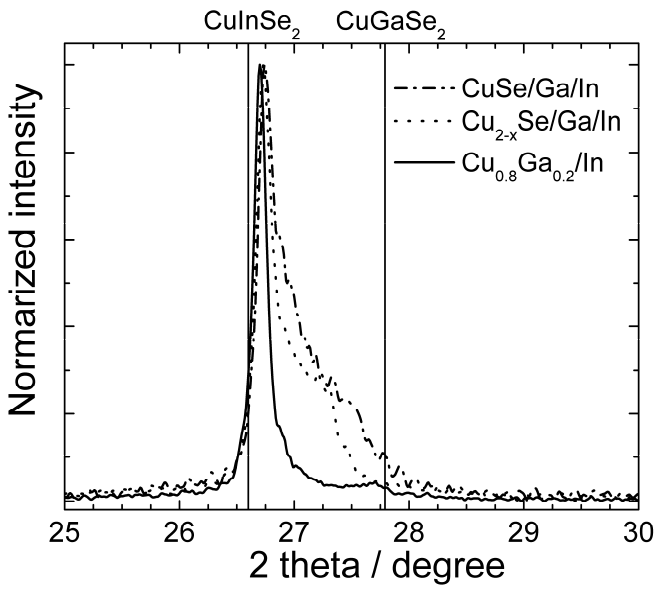


Figure 4. XRD scans of the Cu(InGa)Se_2 (112) peak after 90 min. selenization of CuSe/Ga/In, $Cu_{2-x}Se$/Ga/In, and $Cu_{0.8}Ga_{0.2}$/In precursors. Peak positions of $CuInSe_2$ and $CuGaSe_2$ are also indicated.

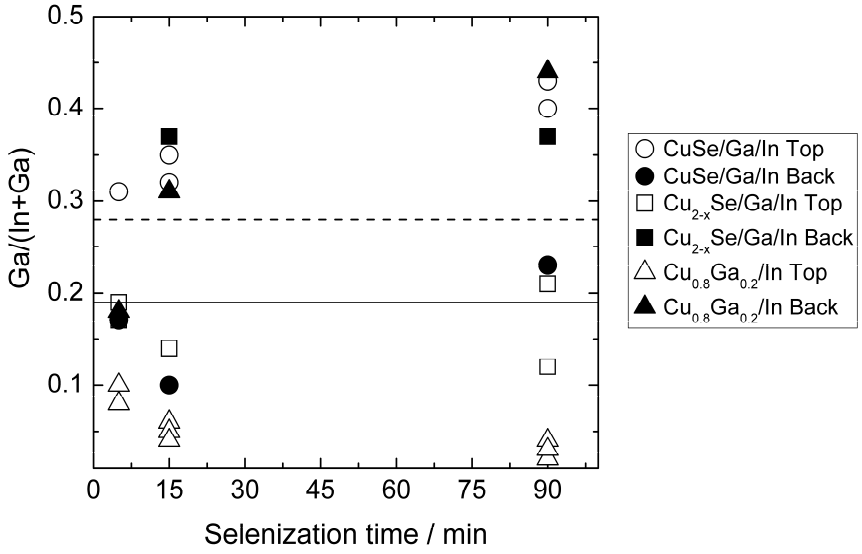


Figure 5. [Ga]/[In+Ga] ratios measured by EDS form the top and back sides of films selenized for different times. The dashed line shows [Ga]/[In+Ga] in the CuSe/Ga/In and $Cu_{2-x}Se$/Ga/In precursors and the solid line shows [Ga]/[In+Ga] in the $Cu_{0.8}Ga_{0.2}$/In precursor.

Device results of the solar cells made from the precursors following 15 min and 90 min selenization treatments are shown in Table II. After 15 min selenization, devices made from CuSe/Ga/In and $Cu_{2-x}Se$/Ga/In precursors showed higher performance than the control. This is consistent with faster selenization rates for the copper selenide precursors compared to $Cu_{0.8}Ga_{0.2}$/In precursor. After 90 min selenization, comparable conversion efficiencies were obtained from CuSe/Ga/In and $Cu_{0.8}Ga_{0.2}$/In precursors but no improvement in V_{OC} was seen.

Table II. Device parameters of solar cells made with 15 or 90 min selenized films.

Precursor	Selenization time (min)	J_{SC} (mA/cm^{-2})	V_{OC} (mV)	FF (%)	η (%)
CuSe/Ga/In	15	30.8	460	44.8	6.4
$Cu_{2-x}Se$/Ga/In	15	16.4	408	42.5	2.9
$Cu_{0.8}Ga_{0.2}$/In	15	18.3	81	26.3	0.4
CuSe/Ga/In	90	28.9	498	61.8	8.9
$Cu_{2-x}Se$/Ga/In	90	19.6	492	60.5	5.8
$Cu_{0.8}Ga_{0.2}$/In	90	36.8	474	50.5	8.8

Figure 6 shows EQE curves of the solar cells. The shift of the long wavelength edge of the EQE towards shorter wavelengths implies a wider bandgap consistent with the increased Ga near the front of the $Cu(InGa)Se_2$ for the films made from the copper selenide precursors.

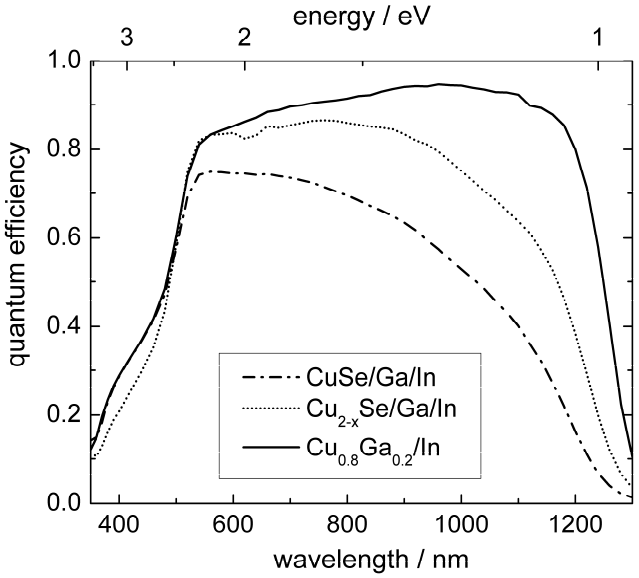
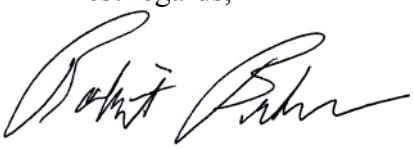


Figure 6. QE curves for devices with CuSe/Ga/In, $Cu_{2-x}Se$/Ga/In, and $Cu_{0.8}Ga_{0.2}$/In precursors after 90 min selenization.

Best regards,



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[1] O. Lundberg, M. Bodegard, J. Malmstrom and L. Stolt, Prog. Photovolt **11**, 77-88 (2003).
[2] W. Shafarman, R. Huang, S. Stephens, Proc. 32nd IEEE PVSC and WCPEC-4, 420-423 (2006).
[3] O. Kluth, B. Rech, L. Houben, S. Wieder, G. Schope, C. Beneking, H. Wagner, A. Loffl and H.W. Schock, Thin Solid Films **351**, 247-253 (1999).